

1012,488



## PATENT SPECIFICATION

NO DRAWINGS

1,012,488

Date of Application and filing Complete Specification: Aug. 23, 1962.

No. 32481/62.

Application made in United States of America (No. 133,773) on Aug. 25, 1961.

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Int. Cl.:—C 01 b // C 11 d

## COMPLETE SPECIFICATION

## Improvements in or relating to Detergent Compositions

## ERRATUM

SPECIFICATION No. 1,012,488  
Amendment No. 1

Page 13, line 85, after "reaction" insert "is"

THE PATENT OFFICE  
26th September 1966

- 25 difference of the so-called "hard-surface" cleaners is that they generally contain little or no organic substituents, i.e., materials, for instance, the alkyl aryl sulfonates, which make up a major portion of other detergents, particularly those used for textile cleaning. In contrast, the "hard-surface" type detergent compositions contain alkaline carbonates, phosphates and sometimes silicates, as the principal ingredients thereof. Perhaps the most widely used of such inorganic ingredients are the alkali metal carbonates, such as soda ash, 30 the sesquicarbonates, typically sodium sesquicarbonate, and the alkali metal orthophosphates, typically trisodium orthophosphate. These materials provide water softening characteristics in the composition as well as 35 some detergency. Additionally, these hard-surface cleaning detergent compositions contain various condensed and crystalline phosphonic, anionic, cationic, and non-ionic surfactant materials. Although, from the standpoint of cleaning efficiency, such a composition has been found to be satisfactory, the thus-formed dry, mechanical mix is subject to some disadvantages. 65
- 70 The principal disadvantage encountered is, of course, that by means of mechanical mixing it is not possible to obtain a completely homogeneous material. Accordingly, no matter how long the various constituents of the detergent composition are mixed and blended, the composition of the final product is not completely homogeneous. These products, upon vibration and shaking over a period of time, as for example, in transit to either wholesale or retail outlets, undergo a phenomenon 75 known as "layering." In such instances, there is a settling of the heavier particles of material in the composition to the bottom portion of 80



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Int. Cl.:—C 01 b // C 11 d

## COMPLETE SPECIFICATION

## Improvements in or relating to Detergent Compositions

We, DIAMOND ALKALI COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of 300 Union Commerce Building, Cleveland 14, Ohio, United States of America, (Assignees of JAMES CLINE MCKENNA, KURT ALBRECHT and JOHN HENRY MCCrackEN), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to detergent compositions and more particularly to detergent compositions having specific applicability as so-called "hard-surface" cleaners, and to the method of preparing such compositions.

Detergent compositions which are applicable for use as "hard surface" cleaners differ from other types of detergents, particularly those used for textile cleaners. The principal difference of the so-called "hard-surface" cleaners is that they generally contain little or no organic substituents, i.e., materials, for instance, the alkyl aryl sulfonates, which make up a major portion of other detergents, particularly those used for textile cleaning. In contrast, the "hard-surface" type detergent compositions contain alkaline carbonates, phosphates and sometimes silicates, as the principal ingredients thereof. Perhaps the most widely used of such inorganic ingredients are the alkali metal carbonates, such as soda ash, the sesquicarbonates, typically sodium sesquicarbonate, and the alkali metal orthophosphates, typically trisodium orthophosphate. These materials provide water softening characteristics in the composition as well as some detergency. Additionally, these hard-surface cleaning detergent compositions contain various condensed and crystalline phos-

phates, e.g. the alkali metal tripolyphosphates, typically sodium tripolyphosphate, and trisodium phosphate, which have good water softening properties. The various pyrophosphates, e.g. sodium pyrophosphate, are also used, which materials generally have a higher detergency than the tripolyphosphates, although their water softening ability is somewhat less. If desired, these compositions may also contain various silicate materials e.g. meta- and ortho-silicates, and liquid silicates, as well as anionic, cationic, and non-ionic surfactant materials, which latter materials are generally present in amounts not in excess of about 5% by weight of the total composition.

Heretofore, it has been the practice to form a mechanical mix of the desired phosphates, e.g. trisodium phosphate and/or sodium tripolyphosphate, and the alkaline carbonate material, e.g. sodium carbonate. In this dry mix is also included any other materials which may be desired, e.g. silicate and/or various anionic, cationic, and non-ionic surfactant materials. Although, from the standpoint of cleaning efficiency, such a composition has been found to be satisfactory, the thus-formed dry, mechanical mix is subject to some disadvantages.

The principal disadvantage encountered is, of course, that by means of mechanical mixing it is not possible to obtain a completely homogeneous material. Accordingly, no matter how long the various constituents of the detergent composition are mixed and blended, the composition of the final product is not completely homogeneous. These products, upon vibration and shaking over a period of time, as for example, in transit to either wholesale or retail outlets, undergo a phenomenon known as "layering." In such instances, there is a settling of the heavier particles of material in the composition to the bottom portion of

the container while the lighter materials remain in a separate layer in the top portion of the container. Thus, when one goes to use a quantity of this material, which is less than the entire contents of the container, the first amount used will be either more or less alkaline than the last-used. This often results in having a product which, for some hard-surface cleaning purposes may be too alkaline, thus injuring the surface to be cleaned, while in other instances, has an insufficient alkalinity to clean the surface completely.

A further disadvantage in the presently used mechanically mixed hard-surface cleaning detergent compositions is in the various, often expensive, manipulative steps required to provide such a composition. For example, it is necessary that the particle size of both the phosphate material and the sodium carbonate material, as well as that of any other solid materials in the composition, be closely controlled so as to be substantially equal in order that a good mechanical mix can be obtained. This, of course, requires various screening operations with resulting over and undersize particles which must be disposed of in some manner. Additionally, the formation of such a mechanically mixed composition requires numerous mixing or agitation steps in order to effect, at least initially, a uniform dispersion of the various components of the composition. These manipulative steps have been found to be somewhat expensive both in terms of the equipment required as well as the time which is necessary to carry them out. Notwithstanding the expensive and time-consuming steps which are required, however, the finished product which is obtained is still subject to a degeneration to a non-homogeneous mixture after normal handling.

It has now been found that these difficulties, as are presently encountered in the production of a mechanically mixed detergent composition, can be overcome by forming this detergent composition by means of a chemical reaction rather than a mechanical dispersion.

According to the present invention, therefore, a method of preparing a dry free-flowing detergent composition comprises dispersing a phosphoric acid in a body of dry solid particles of an alkali metal carbonate-containing material in a proportion in which the  $M_2CO_3:H_3PO_4$  mole ratio ( $M$  being the alkali metal) is at least 1.5:1, in order to effect a chemical reaction therebetween, agitating the resulting mixture while maintaining

it at a temperature not substantially in excess of 104° C. until the reaction is complete, and recovering the resulting dry free-flowing product characterized by an  $M_2O:P_2O_5$  mole ratio greater than 3:1 and a pH, as a 1% weight per volume solution in water, greater than 7.5.

The invention also includes detergent compositions made by the method.

Preferably, the  $M_2CO_3:H_3PO_4$  mole ratio is within the range of 2:1 to 6:1, and the product produced has an  $M_2O:P_2O_5$  mole ratio within the range of 4:1 to 12:1 and a pH, as a 1% weight per volume water solution in water, greater than 9.5.

According to one preferred embodiment of the invention, the acid is an orthophosphoric acid and the alkali metal carbonate-containing material is sodium carbonate. Advantageously, the orthophosphoric acid has an orthophosphoric acid concentration greater than 20% by weight and the sodium carbonate is a granular light ash having a granular size range such that 65 to 100% is retained on a 100 mesh U.S. Tyler screen and at least 92% on a 200 mesh U.S. Tyler screen.

An organic surfactant material is preferably added to an aqueous solution of orthophosphoric acid to produce a solution having an  $H_3PO_4$  content of at least 20% by weight.

According to another preferred embodiment of the invention, the acid is a concentrated phosphoric acid containing a mixture of various phosphoric acids, including pyrophosphoric acid, and the sodium carbonate material is a granular light ash having a granular size range such that 65 to 100% is retained on a 100 mesh U.S. Tyler screen and at least 92% on a 200 mesh U.S. Tyler screen.

In addition to the above-mentioned materials, the detergent composition made by the method of the present invention may also contain various optional components, e.g. silicates; these can comprise the various alkali metal silicates, particularly sodium silicate, including the solid silicates, e.g. sodium ortho, pyro, and meta silicates, as well as the various liquid silicate compositions, e.g. those having an  $M_2O:SiO_2$  ratio within the range of 1:3.3 to 1:1. The organic surfactant material may be non-ionic, anionic or cationic and either in liquid or solid form. Examples of such materials which may be used are found in the following tables, those trade names given in inverted commas being Registered Trade Marks:

## NON-IONIC SURFACTANTS

Trade Name	Manufacturer	Description
"Triton" NE	Rohm & Haas Co.	Alkylated aryl polyether alcohol
"Triton" X-100	Rohm & Haas Co.	Alkylated aryl polyether alcohol
Igepal CO-630	General Dyestuff Co.	Alkyl aryl polyethylene glycol ether
Igepal Ca-630	General Dyestuff Co.	Alkyl aryl polyethylene glycol ether
"Renex" 48	Atlas Powder Co.	Polyoxyethylene ester of mixed fatty and resin acids (Tall oil)
"Renex" 28	Altas Powder Co.	Polyoxyethylene ester of mixed fatty and resin acids (Tall oil)
"Sterox" CD	Monsanto Chem. Co.	Polyoxyethylene ether
"Sterox" SE	Monsanto Chem. Co.	Polyoxyethylenethio ether
"Sterox" SK	Monsanto Chem. Co.	Polyoxyethylenethio ether
Alrosol	Alrose Chem. Co.	Fatty alkylol amine condensate
Alrosol C	Alrose Chem. Co.	Fatty alkylol amine condensate
Alrosol H	Alrose Chem. Co.	Fatty alkylol amine condensate
"Antarox" A-200	Gen. Aniline & Film Co.	Alkyl aryl polyethylene glycol
Cerfak 1300	E. F. Houghton & Co.	Alkyl polyoxyethylene alcohol
Cerfak N-100	E. F. Houghton & Co.	Polyethanolamine fatty acid condensate
Dergon OM	Arkansas Co.	Amino fatty ester
Neutronyx 600	Onyx Oil & Chem. Co.	Aromatic polyglycol ether condensate
"Nonic" 218	Sharples Chemicals, Inc.	Polyethylene glycol tertdodecyl thioether
1011	E. F. Drew & Co.	A secondary amide of lauric acid

## ANIONIC SURFACTANTS

Trade Name	Manufacturer	Description
Naccolene F	Natl. Aniline Div. Allied Chem. & Dye Corp.	Modified alkyl aryl sulfonate
Nacconol NR	Natl. Aniline Div. Allied Chem. Dye Corp.	Alkyl aryl sulfonate
Nacconol LAL	Natl. Aniline Div. Allied Chem. & Dye Corp.	Sodium lorol sulfoacetate
"Santomerse" D	Monsanto Co.	Decyl benzene sodium sulfonate
Ultrawet 30E	Atlantic Refining Co.	Alkyl benzene sodium sulfonate
"Orvus" WA	Proctor & Gamble Co.	Sodium salt of lauryl sulfate
Duponol LS	E. I. du Pont	Technical oleyl sulfate
Duponol SN	E. I. du Pont	Sodium lorol sulfate
Duponol WAT	E. I. du Pont	Triethanolamine salt of alcohol sulfates
Aerosol 18	American Cyanamid Co.	N-octa decyldisodium sulfo succinamate
Alrogei	Alrose Chemical Co.	Fatty amide sulfate
"Antaron" L-245	General Aniline & Film	Sodium palmitoyl methyltaurate
Cyclopon A	General Dyestuffs Corp.	$C_{15}H_{31}CON(CH_3)C_3H_7SO_3Na$
Igepon T	General Dyestuffs Corp.	$C_{17}H_{33}CON(CH_3)C_2H_5SO_3Na$
"Lissapol"LS	Imperial Chem. Ind.	Sodium oleyl p-anisidine sulfonate
Michelene DLC	M. Michel & Co.	Mixture of $CH_3(CH_2)_{11}-C_6H_4-SO_3Na$ and $CH_3(CH_2)_x-CH_2-C(=O)-N(C_2H_4OH)-C_2H_4OH$
Miranol HM	Miranol Chem. Co.	Lauroyl imidazolene
Pactivex	Publicker Ind., Inc.	Sodium dodecyl toluene sulfonate
"Triton" W-30	Rohm & Haas Co.	Sodium salt of alkylated aryl polyether sulfate

## CATIONIC SURFACTANTS

Trade Name	Manufacturer	Description
Hyamine 1622	Rohm & Haas Co.	Di-isobutyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride
Onyxide	Onyx Oil & Chem.	Alkenyl dimethyl ethyl ammonium bromide
"Roccal"	Winthrop-Stearns, Inc.	Alkyl dimethyl benzyl ammonium chloride
Alro Amines-C,O-S	Alrosc Chem. Co.	$\begin{array}{c} \text{N}-\text{CH}_3 \\   \\ \text{CH}_3-(\text{CH}_2)_n-\text{C} \\   \\ \text{N}-\text{CH}_2 \\   \\ \text{R} \end{array}$
Amine 220	Carbide & Carbon Chem. Corp.	$\begin{array}{c} \text{R}-\text{C}-\text{N}-\text{CH}_2\text{CH}_2\text{OH} \\    \quad   \\ \text{N}-\text{CH}_2-\text{CH}_3 \end{array}$
"Arquad" Series	Armour & Co.	$\text{R}-\text{N}(\text{CH}_3)_3 \text{Cl}$ ; $\text{R} = 12-18$
Cetab	Rhodes Chem. Co.	Cetyl trimethyl ammonium bromide — $\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3 \text{Br}$
Emulsept	Emulsol Corp.	$\text{CH}_3(\text{CH}_2)_n-\text{COOCH}_2\text{CH}_2\text{NHCOCH}_2\text{N}-\text{Cl}$ $\quad \quad \quad  $ $\quad \quad \quad \text{C}_6\text{H}_5$
Germ-i-tol	Fine Organics, Inc.	Dimethyl benzyl lauryl ammonium chloride
"Octab"	Rhodes Chem. Co.	Octadecyl dimethyl benzyl ammonium chloride — $\text{C}_{18}\text{H}_{37}(\text{CH}_2)_2\text{N}(\text{C}_6\text{H}_5\text{CH}_2)_2 \text{Cl}$
"Oronite" Quaternary-ATM50	Oronite Chem. Co.	N-alkyl benzyl N—N—N trimethyl ammonium chloride
LPC	Hooker Elec.-Chem.	Lauryl pyridinium chloride — $\text{C}_6\text{H}_5\text{N}(\text{C}_{12}\text{H}_{25})_3 \text{Cl}$

The composition of the present invention is prepared by reacting an alkali metal carbonate-containing material with phosphoric acid, the amounts of these reactants being sufficient to form a product having a mole ratio of  $M_2O:P_2O_5$ , which is greater than 3:1. This is done by adding the phosphoric acid to the dry alkali metal carbonate-containing material, typically sodium carbonate, with agitation, in an amount of at least 1.5 moles of sodium carbonate to 1 mole of  $H_3PO_4$ . The addition of the phosphoric acid to the sodium or other alkali metal carbonate is made over a sufficiently long period of time so as to provide complete mixing and reaction of these materials and to prevent the formation of lumps in the reaction mixture. The actual addition time will, of course, depend upon the type of mixing apparatus which is used so that, with more efficient mixing, a shorter addition time can be used. It is to be appreciated that, although lumping in the reaction mixture is not desired, if lumps do occur, the product can still be used by subjecting it to a grinding or crushing operation so as to reduce the lumps to a usable size.

It has not been found that the reaction temperature is extremely critical or that it must be maintained within narrow limits in order to produce the product of the present invention. Thus, it has not been found to be necessary either to heat the reaction mixture or to cool it in order to maintain some desired reaction temperature. It has been found however, that the reaction temperature should not exceed  $104^\circ C$  for any prolonged period of time during the reaction. When temperatures greater than  $104^\circ C$ . are maintained over a long period, it has been found that there is an excessive reaction loss, in terms of water and carbon dioxide given off, which loss is desirably avoided, if possible.

The composition produced by this reaction contains at least one phosphate, having the formula:



where M is an alkali metal, x and y are positive integers greater than 0, the sum of which is 3 and a is a number from 0 to 2, and at least one alkali metal compound selected from the group consisting of carbonates, bicarbonates, sesquicarbonates, and mixtures thereof. The phosphate which has been found to predominate in this composition is the di-alkali metal acid phosphate, e.g.,  $Na_2HPO_4$ , although the mono-alkali metal acid phosphate, e.g.  $NaH_2PO_4$ , is also formed. These phosphates have been found to be either anhydrous, mono- or di-hydrated, with the dihydrate appearing to predominate over the mono-hydrate. Thus, the predominant phosphate in the present composition is  $Na_2HPO_4$ , or its di-hydrate,  $Na_2HPO_4 \cdot 2H_2O$ , with

lesser quantities being formed of the mono-sodium acid phosphate,  $NaH_2PO_4$ , or its dihydrate,  $NaH_2PO_4 \cdot 2H_2O$ . It is to be appreciated, of course, that whether the anhydrous or hydrated form of the phosphate is produced will depend upon the amount of water available in the reaction mixture.

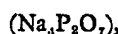
The alkali metal compound of the composition of the present invention is sodium carbonate, sodium sesquicarbonate, sodium bicarbonate, or mixtures of these materials. Inasmuch as the reaction mixture contains an excess of the sodium carbonate in order to provide the necessary  $M_2O:P_2O_5$  ratio of greater than 3:1, there would, obviously, be some sodium carbonate in the product, the amount depending upon the initial starting ratio of sodium carbonate to phosphoric acid. Although it is not certain, it is believed that, in the reaction which takes place, carbon dioxide is given off which then reacts with the excess sodium carbonate to form sodium bicarbonate. Where water is also present in the reaction mixture, there will be a further reaction of the sodium bicarbonate with any excess sodium carbonate to form sodium sesquicarbonate or trona. Thus, depending upon the amount of sodium carbonate which is initially used in the reaction mixture, as well as the amount of water present, the final product of the present invention will contain at least one of the alkali metal compounds selected from the carbonates, bicarbonates, and sesquicarbonates and, generally, will contain more than one of these materials, the most likely combination being the carbonate and the sesquicarbonate. It is to be noted, once again, that the product of the present invention is the result of a chemical reaction so that the alkali metal compound will be intimately combined with the phosphates and will not be merely a mechanical mixture.

In the preparation of the composition of the present invention, any type of phosphoric acid may be used. Although the orthophosphoric acid ( $H_3PO_4$ ) is the most common and least expensive of the phosphoric acids, solutions of the various other phosphoric acids, e.g. pyrophosphoric acid ( $H_4P_2O_7$ ), tripolyphosphoric acid ( $H_5P_3O_{10}$ ), and metaphosphoric acid ( $HPO_3$ ), may also be used. In addition to these, more concentrated phosphoric acids, which are mixtures of the various forms of phosphoric acid, may also be used. Exemplary of such materials is a concentrated phosphoric acid, sold by Monsanto Company, under the name "Phospholeum." This acid has a  $P_2O_5$  content equivalent to 105%  $H_3PO_4$ , and has the following typical analysis:

orthophosphoric acid ( $H_3PO_4$ )	58%	
pyrophosphoric acid ( $H_4P_2O_7$ )	38%	
tripolyphosphoric acid ( $H_5P_3O_{10}$ )	3.5%	125
higher polyphosphoric acids, such as $H_6P_4O_{13}$ , $H_7P_5O_{17}$ ( $HPO_3$ ) <sub>n</sub>	0.5%	

all of the above being percent by weight of the total composition.

In actual practice the use of this more concentrated phosphoric acid has been found to give definite advantages over the other phosphoric acids, e.g. orthophosphoric acid. Although the more concentrated phosphoric acid is slightly more expensive than orthophosphoric acid, because of its greater  $P_2O_5$  content, its cost, based on the  $P_2O_5$  content, is about the same as orthophosphoric acid. Additionally, it has been found that, when this more concentrated phosphoric acid is reacted with the soda ash in the method of the present invention, there is substantially no reversion of the pyrophosphoric acid content of the acid to the ortho form. Thus, the product produced contains tetrasodium pyrophosphate



which material is very desirable in a detergent composition because of its sequestering, dispersing and deflocculating action. Accordingly, by the use of a more concentrated phosphoric acid, which is a mixture of various forms of phosphoric acid, a detergent product is obtained, which contains as a part of the chemical reaction product, a sequestering agent, thus making it unnecessary to add such a material to the composition and combine it by means of mechanical mixing.

The concentration of the phosphoric acid used, whether it is a more concentrated mixture of various forms of phosphoric acid or not, has not been found to be extremely critical. Thus, when using orthophosphoric acid, for example, the commercial grade of 85% phosphoric acid may be used. Similarly, various more dilute acids may also be used, e.g. 65%, 45%, and 25%. Inasmuch as it is desirable that the product, prepared by the present method, is dry and free-flowing, the phosphoric acid concentration should not be so low that excessive quantities must be added to the reaction mixture when the desired  $P_2O_5$  content is obtained. As has been set forth hereinabove the amount of water present in the reaction mix is the principal determining factor as to whether the anhydrous or hydrated forms of the alkali metal phosphates are produced, and also whether the sodium bicarbonate produced will combine with the sodium carbonate to produce sodium sesquicarbonate. Inasmuch as any water, present in the reaction mix in excess of that required to perform the above two functions, will tend to make the final product somewhat tacky, thus necessitating an additional drying step, it is preferred that the phosphoric acid used shall not have a concentration less than 20% by weight. Again, it will be appreciated, that the choice as to the concentration of the phosphoric acid which is used will be dictated according to

the composition which is desired in the final product. Where a detergent composition is required, which contains a hydrated sodium phosphate, or which contains large amounts of trona, the more dilute phosphoric acid will be used. Similarly, where the anhydrous forms of the sodium phosphate are required, or smaller amounts of trona, the converse is true. It is believed that those skilled in the art will be able to determine in each instance the type of composition which is required and, hence, the concentration of phosphoric acid which should be used.

The alkali metal carbonate-containing material, which is reacted with the phosphoric acid to obtain the composition of the present invention, may be the alkali metal carbonate itself, e.g. sodium carbonate, or it may be a compound containing the alkali metal carbonate, e.g. sodium sesquicarbonate. Generally, for reasons of cost consideration, it is preferred to use the less expensive alkali metal carbonates, e.g. sodium carbonate, rather than the more expensive sesquicarbonate. Any of the available forms of the alkali metal carbonate, e.g., sodium carbonate, may be used, including the so-called "light ash" and "dense ash." These materials are, of course, sodium carbonates which differ only in particle structure and bulk density. Additionally, a new and unique form of sodium carbonate, having a granular particle configuration but a low bulk density, may also be used. This material has a bulk density comparable to that of light ash, but, unlike light ash, which is extremely fine, its particle configuration is granular, very similar in size to that of dense ash. In view of the unique characteristics of this material, which characteristics will be referred to in more detail hereinafter, it is the preferred form of sodium carbonate for use in the method of the present invention. For the sake of convenience, this material will henceforth be referred to as granular light ash.

This preferred granular light ash, and its method of preparation, are described in British Application No. 24152/62. Serial No. 1,005,400.

As is set forth in this copending application the granular light soda ash is prepared by mixing a hydrated sodium carbonate with sodium bicarbonate in a proportion of bicarbonate to hydrated carbonate, in terms of alkali metal carbonate equivalents, substantially within the range of 5:1 to 1:2, so as to form substantial amounts of sodium sesquicarbonate in the mixture. Thereafter, the mixture is rapidly heated to a temperature above that at which decomposition of the bicarbonate and sesquicarbonate began, and the carbonate becomes anhydrous. This temperature is maintained for a sufficient period of time to effect decomposition of the mixture while carbon dioxide and water, evolved from



the mixture during the heating, are removed. The sodium carbonate product thus produced is then recovered. This product is characterized by larger particles than those obtained by the calcination of an alkali metal bicarbonate alone and a bulk density within the range of 25 to 45 lbs. per cubic foot. This sodium carbonate product is further characterized by having spheroidal particles of the size such that 65 to 100% is retained on a 100 mesh U.S. Tyler screen, and upwards of 92% is retained on a 200 mesh U.S. Tyler screen.

The use of this granular light ash has been found to be particularly advantageous in forming the present composition in that, by its use, a dry granular composition can be formed even when using relatively poor mixing to combine the carbonate material and the phosphoric acid. Additionally, this granular light ash has exceptional absorption characteristics which are particularly advantageous when liquid silicates and organic surfactants are to be included in the composition. In this regard it has been found that liquid silicates and non-ionic, cationic, and anionic surfactants can be absorbed by this granular light ash in amounts up to as high as 30% or 35% by weight of the total composition, i.e., the granular light ash plus the silicate or surfactant. Accordingly, where these materials are desired in the present detergent composition, the surfactants can be admixed with the phosphoric acid prior to the time it is added to the granular light ash, and the resulting mixture then combined with the ash. In the case of the silicates they can be added subsequently to the phosphoric acid. In this way, the liquid silicates and/or organic surfactants are absorbed by the granular light ash and the phosphoric acid reacts therewith to form the product of the present invention in dry, granular form, having the silicate and surfactants intimately dispersed therein. Thus, the necessity for any mechanical mixing step is completely eliminated. This granular light ash is further advantageous in view of its rapid solubility in water as compared to conventional light ash and dense ash. For example, comparing the solubility rate of 60 g. of material in 200 ml. of water, the granular light ash dissolves in 22 seconds, while 26 seconds are required for conventional light ash, and 47 seconds for conventional dense ash. It is for these reasons that the granular light ash, as described in British Application No. 24152/62, Serial No. 1,005,400 is the preferred alkali metal carbonate material for forming the detergent composition of the present invention.

As has been set forth hereinabove, the alkali metal carbonate-containing material, preferably the granular light ash, and a phosphoric acid, are combined in amounts which will give a reaction mixture, and hence, a product, having a mole ratio of  $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$ ,

which is greater than 3:1. In order to attain this mole ratio of  $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$ , it is necessary that the initial reactants are combined in an amount so that the mole ratio of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) to phosphoric acid ( $\text{H}_3\text{PO}_4$ ) is greater than 1.5:1. A preferred ratio of sodium carbonate to phosphoric acid ( $\text{H}_3\text{PO}_4$ ) is within the range of 3:1 to 6:1. Although ratios of sodium carbonate to phosphoric acid, which are greater than 6:1, may be used, the product produced from such ratios has such a high alkalinity that it is not usable for many applications. Accordingly, the preferred upper ratio of sodium carbonate to phosphoric acid ( $\text{H}_3\text{PO}_4$ ) is 6:1, although this is not to be taken as limiting.

It is believed that those skilled in the art will appreciate that, where the lower ratios of sodium carbonate to phosphoric acid are used, there will, obviously, be less excess sodium carbonate in the reaction mixture. Accordingly, this means that less water can be tolerated in the reaction mixture and still obtain a product which is not tacky. In these circumstances, it will be necessary to use the more concentrated phosphoric acids since, as has been set forth hereinabove, additional quantities of water are introduced into the reaction mixture when using the more dilute phosphoric acid. Thus, when using a sodium carbonate to phosphoric acid ( $\text{H}_3\text{PO}_4$ ) mole ratio of about 2:1, it is not feasible to use a phosphoric acid having a concentration of less than 65%, and still obtain a dry, granular product. In contrast, when the mole ratio of sodium carbonate to phosphoric acid ( $\text{H}_3\text{PO}_4$ ) used is 6:1, phosphoric acid concentration as low as 25%, or less, can be used without adversely affecting the free-flowing characteristics of the product produced. Again, it will be appreciated by those skilled in the art that the mole ratio of sodium carbonate to phosphoric acid, which is used, will depend upon the constituents which are desired in the detergent product. Where, for example, a product is desired having only a small amount of sodium carbonate or sodium sesquicarbonate, the lower mole ratios of sodium carbonate to phosphoric acid, e.g. 2:1 or 3:1, will be used. Alternatively, where large amounts of sodium carbonate and/or sesquicarbonate are desired in the product, the higher ratios of sodium carbonate to phosphoric acid, e.g. 5:1 or 6:1, will be used. It is believed that those skilled in the art will readily be able to determine the mole ratio of sodium carbonate to phosphoric acid which is desired, in combination with the concentration of phosphoric acid which is to be used, depending on the substituents which are desired in the finished product.

In order that those skilled in the art may better understand the present invention and the manner in which it may be practised, the following specific examples are given.

In the following examples the phosphoric acid used is orthophosphoric acid of varying concentrations. The procedure followed consisted in cooling the orthophosphoric acid to 0° C. in a beaker with dry ice. The temperature of the sodium-carbonate-containing material used was room temperature, i.e., 24° C. In Examples 1 to 12 the sodium carbonate-containing material was the granular light ash prepared in accordance with the procedure set forth in British Application No. 24152/62. Serial No. 1,005,400. In Examples 13 to 16 the sodium carbonate material used was commercial light ash, having a bulk density of 34.2 lbs. per cu. ft., while Examples 17 and 18 used commercial dense ash, having a bulk density of 61.2 lbs. per cu. ft. The bulk density of the granular light ash used in Examples 1 to 12 was 33.7 lbs. per cu. ft. The sodium carbonate material was placed in a Patterson-Kelley twin shell blender (8 qt. liquids-solids model) just prior to reaction time. This blender is manufactured by the Patterson-Kelley Co., Inc., of E. Stroudsburg, Pa. It consists of a V-shape container, provided with covered openings in the end of each leg of the V, through which the material to be blended is charged, and a discharge opening in the apex of the V. The blender is supported by a shaft which passes through both legs of the V about three-fourths of the way up the legs from the apex. The entire blender rotates around this shaft. Additionally, a mixing bar is provided on this shaft, which rotates independently of the

blender and through which liquid components are added to the dry materials in the blender. When the sodium carbonate material was placed in the blender and the covers sealed, rotation of the blender and the mixing bar was begun. The respective rotational speeds of the blender and mixing bar were 35 rpm and 1700 rpm. The phosphoric acid of the desired concentration was fed into the sodium carbonate material through 0.01" openings in the mixing bar. After the phosphoric acid addition was completed, the temperature of the hot product was measured. Mixing of the product was then continued for about 20 minutes so as to provide for partial cooling and absorption of water vapor. The weight of the product was then recorded and the percent weight reaction loss determined.

The amounts of the reactants which were used were determined by the mole ratio of  $\text{Na}_2\text{CO}_3:\text{H}_3\text{PO}_4$ . For each mole of  $\text{Na}_2\text{CO}_3$ , 106 g were used. For each mole of  $\text{H}_3\text{PO}_4$ , 98 g were used. Where the phosphoric acid used had a concentration of 85%, 115.3 g. were used for each mole of  $\text{H}_3\text{PO}_4$  required. Similarly, when using acid concentrations of 65, 45 and 25 percent, the following quantities were used for each mole of  $\text{H}_3\text{PO}_4$  required:

65%	150.8 g.
45%	217.8 g.
25%	392.0 g.

Using this procedure, the following runs were made:

Example	Mole Ratio $\text{Na}_2\text{CO}_3$ : $\text{H}_3\text{PO}_4$	$\text{H}_3\text{PO}_4$ Concentra- tion %	$\text{H}_3\text{PO}_4$ Addition Time Min.	Final Tempera- ture of Prod. °C.	Reaction Loss % by Wt.	PRODUCT COMPOSITION —		
						$\text{Na}_2\text{O}$		Actual Adj. for React. Loss
						Theor- etical	Actual	
1	2:1	85	9	95	9.83	37.9	42.5	38.3
2	2:1	66.73	6	86	9.36	34.2	38.1	34.5
3	3:1	85	6.5	99	5.78	42.9	46.4	43.7
4	3:1	65.63	5	98	4.58	39.7	42.2	40.2
5	3:1	45	5	92	2.73	34.7	36.0	35.0
6	4:1	85	6.5	97	3.56	46.0	48.0	46.3
7	4:1	65.63	6	99	2.80	43.1	44.6	43.4
8	4:1	45	7	92	2.01	38.6	39.6	38.8
9	6:1	85	6	90	0.04	49.5	51.0	51.0
10	6:1	65	5.5	91	1.21	47.3	48.3	47.7
11	6:1	45	5.5	92	0.34	43.6	44.5	44.3
12	6:1	25	5	88	0.84	36.2	36.7	36.4
13	3:1	45	6	102	2.33	34.7	35.7	34.9
14	3.23:1	45	5.5	95	1.61	35.7	36.9	36.3
15	4:1	45	4.5	96	1.50	38.6	39.8	39.2
16	6:1	45	4.5	93	0.28	43.6	44.6	44.5
17	4:1	45	9	96	2.61	38.6	39.8	38.8
18	6:1	45	5.5	93	1.68	43.6	44.6	43.9

/ BY WEIGHT

P <sub>2</sub> O <sub>5</sub>			CO <sub>2</sub>			H <sub>2</sub> O		Mole Ratio Na <sub>2</sub> O: P <sub>2</sub> O <sub>5</sub> in Prod.	pH as a 1% weight per volume solution in water	Bulk Density lb/ft <sup>3</sup>
Theor- etical	Actual	Actual Adj. for React. Loss	Theor- etical	Actual	Actual Adj. for React. Loss	Theor- etical as free H <sub>2</sub> O	Total			
21.7	24.5	22.1	26.9	23.0	20.7	5.3	5.1	4:1	9.64	49.0
20.1	22.9	20.8	24.3	18.9	17.2	13.8	12.7	4:1	9.43	43.6
16.4	16.3	15.4	30.5	29.1	27.4	4.0	3.8	6:1	9.96	44.9
15.3	17.8	16.9	28.1	28.0	26.7	11.1	9.3	6:1	9.82	42.5
13.3	14.0	13.6	24.6	23.4	22.8	22.4	21.8	6:1	9.78	39.8
13.2	14.4	13.9	32.6	30.0	28.9	3.2	2.9	8:1	10.13	45.2
12.5	13.1	12.8	30.6	30.6	29.7	9.0	8.5	8:1	10.06	39.0
11.1	12.1	11.8	27.4	27.3	26.7	18.7	17.4	8:1	9.97	36.8
9.4	9.9	9.9	35.2	34.3	34.3	2.3	2.2	12:1	10.39	42.5
9.1	9.6	9.5	33.5	34.2	33.8	6.7	5.7	12:1	10.22	41.8
8.3	8.9	8.8	30.9	31.6	31.5	14.0	12.6	12:1	10.13	39.1
6.9	7.8	7.7	25.7	25.9	25.7	28.6	27.0	12:1	1.011	32.6
13.3	14.3	14.0	24.6	24.7	24.1	22.4	20.9	6:1	9.73	42.4
12.7	13.8	13.6	25.4	26.3	25.9	21.4	19.1	6.46:1	9.77	32.9
11.1	11.9	11.7	27.4	27.9	27.5	18.7	16.9	8:1	9.99	27.5
8.3	8.8	8.8	30.9	31.5	31.4	14.0	12.2	12:1	10.23	30.1
11.1	11.7	11.4	27.4	26.8	26.1	18.7	19.2	8:1	10.17	44.1
8.3	8.5	8.3	30.9	31.0	30.5	14.0	14.0	12:1	10.37	50.8

All of the products obtained in the above examples were dry and free-flowing. These products obtained in Examples 1 to 12, which used the granular light ash as a starting material, were also granular in form. Similarly, the products obtained in Examples 13, 17 and 18 were also granular in form. The products obtained in Examples 14 to 16 were in the form of a powder. X-ray analysis of all of these products shows that they contain  $\text{Na}_2\text{HPO}_4$ ,  $\text{Na}_2\text{CO}_3$ , and sodium sesquicarbonate, in varying concentrations depending upon the initial mole ratio of  $\text{Na}_2\text{CO}_3:\text{H}_3\text{PO}_4$ . Additionally, depending upon the concentration of phosphoric acid used, both the anhydrous and the dihydrated forms of the  $\text{Na}_2\text{HPO}_4$  ( $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ ) were present. It is to be noted that, in the analysis of the product composition, the weight percentages of the  $\text{Na}_2\text{O}$ ,  $\text{P}_2\text{O}_5$ , and  $\text{CO}_2$  were obtained by experimental analysis. With regard to the water in the composition the column, headed "Theoretical-as free  $\text{H}_2\text{O}$ " refers to the amount of water which should be present,

based upon the water added to the initial reaction mixture. The column, headed "Total  $\text{H}_2\text{O}$ ," is a calculated value arrived at by subtracting the sum of the anhydrous components of the mixture, calculated as  $\text{Na}_2\text{HPO}_4$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{NaHCO}_3$ , from 100%. This total amount of water represents the water which is held in the composition as water of hydration for the components, as well as any free water which may be absorbed in the product.

#### EXAMPLE 19.

By way of comparison an additional run is made, using the procedure as set forth hereinabove with the granular light ash as the sodium carbonate material, and using 85% orthophosphoric acid. The mole ratio of  $\text{Na}_2\text{CO}_3:\text{H}_3\text{PO}_4$  is 1:1. The phosphoric acid is added over a period of 12 minutes, and the final temperature of the product is 95° C. There is a reaction loss in the experiment of 19.2%. The mole ratio of  $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$  in the product is 2:1, and the product has the following composition in percent by weight:

Na <sub>2</sub> O			P <sub>2</sub> O <sub>5</sub>			CO <sub>2</sub>		H <sub>2</sub> O		
Theor- etical	Actual	Actual Adj. for Reaction Loss	Theor- etical	Actual	Actual Adj. for Reaction Loss	Theor- etical	Actual	Actual Adj. for Reaction Loss	Theor- etical as Free H <sub>2</sub> O	Total
28.0	34.9	28.2	32.1	40.6	32.8	19.9	4.42	3.57	7.8	12.8

The pH as a 1% weight per volume solution of this product in water is 7.44, and the product has a bulk density of 48.1 lbs. per cubic foot. Although the product of this reaction is granular in form, it is quite damp and no free-flowing.

By a comparison of this example with the above Examples 1 to 18 it is seen that, when the product has a mole ratio of  $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$ , which is less than about 3:1, the pH of a water solution of this product is sufficiently non-alkaline as to greatly limit the use of the material. Additionally, it is seen that, unlike the products of Examples 1 to 18, the material produced hereinabove is not free-flowing.

#### EXAMPLE 20.

An additional experiment is made, using the apparatus as set forth for the preceding examples. In this experiment the sodium carbonate material is the granular light ash and the phosphoric acid is a concentrated phosphoric acid having the following composition in percent by weight:

$\text{H}_3\text{PO}_4$	58%
$\text{H}_4\text{P}_2\text{O}_7$	38%
$\text{H}_5\text{P}_3\text{O}_{10}$	3.5%
$(\text{HPO}_3)_n$	0.5%

These materials are reacted in a mole ratio of  $\text{Na}_2\text{CO}_3:\text{H}_3\text{PO}_4$  of 2:1, to give a product having an  $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$  ratio of 4:1. 4,000 g. of the granular light ash are used to which are added 1,762 g. of the concentrated phosphoric acid. The initial temperature of the granular light ash is 24° C. and that of the phosphoric acid is 21° C. The phosphoric acid is added over a period of 26 minutes and the final temperature of the product is 104° C. The reaction loss for this product is 9.79%. The theoretical composition of this product is as follows:

$\text{Na}_2\text{HPO}_4$	25.70%	90
$\text{Na}_4\text{P}_2\text{O}_7$	17.36%	
$\text{Na}_5\text{P}_3\text{O}_{10}$	1.53%	
$(\text{NaPO}_3)_n$	0.20%	
$\text{Na}_2\text{CO}_3$	35.19%	
$\text{H}_2\text{CO}_3$	20.02%	95

Experimental analysis of the  $\text{Na}_4\text{P}_2\text{O}_7$  content of this product indicates that the actual content of this component is 19.60% before being adjusted for the reaction loss, and is equal to 17.70% after being adjusted for the reaction loss. This value corresponds quite closely to the theoretical amount of 17.36%. The pH

as a 1% weight per volume solution of the product of this example in water is 9.71, and the bulk density of the product is 41.3 lbs. per cu. ft. as compared to a bulk density of 33.7 lbs. per cu. ft. for the granular light ash. The product obtained is dry, in granular form, and is free-flowing.

From this example it is seen that, when a concentrated phosphoric acid, made up of a mixture of various forms of phosphoric acid, including pyrophosphoric acid, is used in the method of the present invention, there is no reversion of the pyrophosphate in the composition to the orthophosphate form.

#### EXAMPLE 21.

111 g. of a non-ionic surfactant, "Triton" (R.T.M.) X-100 (alkylated aryl polyether alcohol) is mixed with 712 ml. of water. To this is added 518 ml. of a 75%  $H_3PO_4$ , and the resulting mixture cooled to 10° C. Using the procedure and apparatus as set forth for Examples 1 through 18, the phosphoric acid solution is added to 4,000 g. of the granular light ash. The resulting composition was found to be dry and free-flowing, having an  $Na_2O$  content of 42% by weight, a  $P_2O_5$  content of 8% by weight, and a non-ionic surfactant content of 2% by weight.

Comparative cleaning tests with this product and commercially available solid and liquid hard surface cleaners showed a decided advantage, in terms of cleaning power for the present composition over the other commercially available compositions tested.

#### EXAMPLE 22.

The procedure of the preceding Example is repeated with the exception that the initial reactant composition consists of 4,000 g. of the granular light ash, 1,540 g. of 40%  $H_3PO_4$ , 70 g. of the "Triton" (R.T.M.) X-100, and 120 g. of dodecyl benzene sulfonic acid. These materials are reacted, using the procedure and apparatus of the preceding example. The resulting product is found to have an  $Na_2O:P_2O_5$  mole ratio of 12:1 and is a dry, granular free-flowing composition. Comparative washing tests, using this product and commercially available solid and liquid hard surface cleaners showed that the composition of this example is superior in cleaning power to the other cleaners tested.

From the foregoing, it has been shown that, by the method of the present invention, a detergent composition can be prepared, which composition is at least equal in cleaning power to other commercially available hard surface cleaners. The composition of the present invention has been found to be a granular, free-flowing product, having the various constituents thereof intimately and homogeneously dispersed throughout the composition. The homogeneous characteristics of the present

composition are the result of the fact that this composition is obtained by means of a chemical reaction, rather than by mere mechanical mixing.

It is to be understood that, although the invention has been described with specific reference to particular embodiments thereof, it is not to be so limited, since changes and alterations therein may be made which are within the full intended scope of this invention as defined by the appended claims.

#### WHAT WE CLAIM IS:—

1. A method of preparing a dry free-flowing detergent composition, which comprises dispersing a phosphoric acid in a body of dry solid particles of an alkali metal carbonate-containing material in a proportion in which the  $M_2CO_3:H_3PO_4$  mole ratio (M being the alkali metal) is at least 1.5:1, in order to effect a chemical reaction therebetween, agitating the resulting mixture while maintaining it at a temperature not substantially in excess of 104° C. until the reaction complete, and recovering the resulting dry free-flowing product characterised by an  $M_2O:P_2O_5$  mole ratio greater than 3:1 and a pH, as a 1% weight per volume solution in water, greater than 7.5.

2. A method according to claim 1, in which the  $M_2CO_3:H_3PO_4$  mole ratio is within the range of 2:1 to 6:1, and the product produced has an  $M_2O:P_2O_5$  mole ratio within the range of 4:1 to 12:1 and a pH, as a 1% weight per volume solution in water, greater than 9.5.

3. A method according to claims 1 or 2, in which the acid is an orthophosphoric acid and the alkali metal carbonate-containing material is sodium carbonate.

4. A method according to claim 3, in which the orthophosphoric acid has an orthophosphoric acid concentration greater than 20% by weight and the sodium carbonate is a granular light ash having a granular size range such that 65 to 100% is retained on a 100 mesh screen and at least 92% on a 200 mesh U.S. Tyler screen.

5. A method according to claim 3 or 4, in which an organic surfactant material is added to an aqueous solution of orthophosphoric acid to produce a solution having an  $H_3PO_4$  content of at least 20% by weight.

6. A method according to claim 1 or 2, in which the acid is a concentrated phosphoric acid containing a mixture of various phosphoric acids, including pyrophosphoric acid, and the sodium carbonate material is a granular light ash having a granular size range such that 65 to 100% is retained on a 100 mesh screen and at least 92% on a 200 mesh U.S. Tyler screen.

7. A method of preparing a dry free-flowing detergent composition, substantially as de-

scribed with reference to the foregoing  
Examples.

8. A dry free-flowing detergent composition, when prepared by a method according  
5 to any preceding claim.

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